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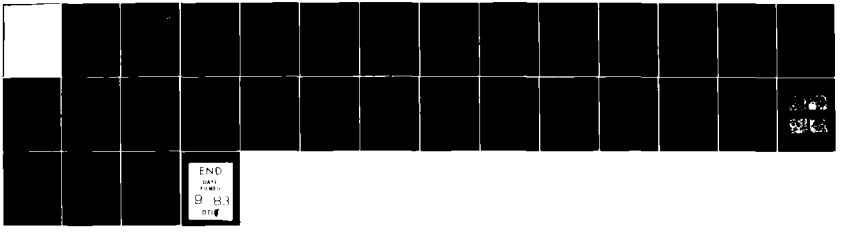

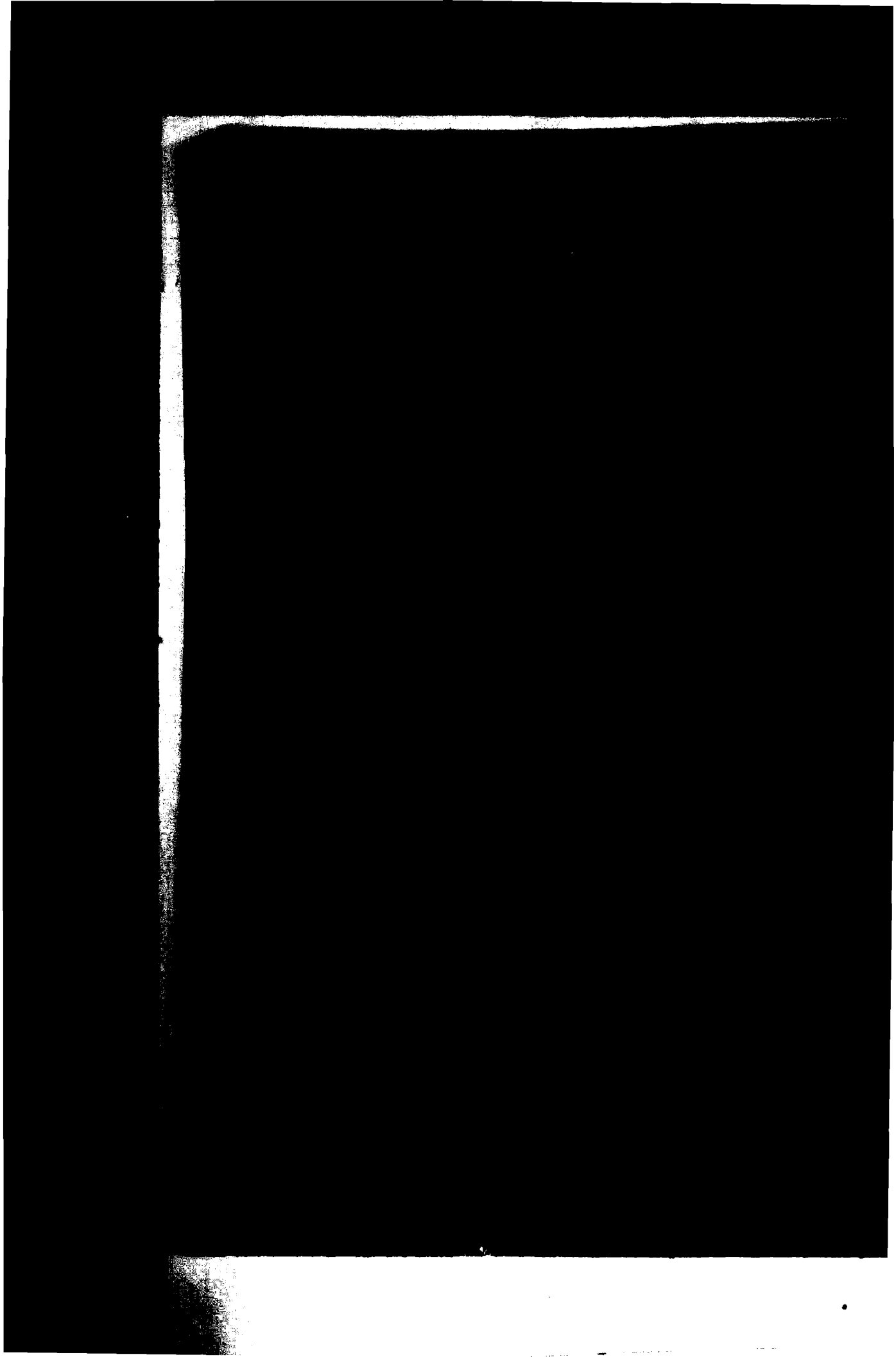

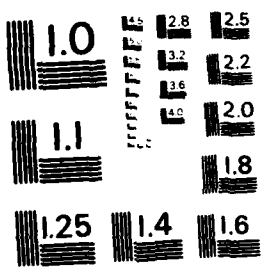

MRL-R-871

AR-003-060

DEPARTMENT OF DEFENCE

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MATERIALS RESEARCH LABORATORIES

MELBOURNE, VICTORIA

REPORT

MRL-R-871

POTASSIUM BENZOATE FOR PYROTECHNIC WHISTLING COMPOSITIONS: ITS SYNTHESIS AND CHARACTERIZATION AS AN ANHYDROUS SALT

D.J. Whelan and P.P. Elischer

Approved for Public Relsease

FEBRUARY, 1983

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Potassium benzoate is one of the ingredients in the formulation SR 136 Whistling Composition. However, some ambiguity exists in the chemical literature as to its hydration state. In this investigation, it was established that potassium benzoate crystallizes from water as colourless plates containing no water of crystallization and it does not appear to take up water from its environment. Its DSC thermogram, over the temperature range 310 K - 750 K, consists of a single, sharp and symmetrical endotherm, occurring near 714 K and probably due to melting, the heat of this reaction being ca 213 J g^{-1} (50.9 cal g^{-1}). It can be prepared from stoichiometric amounts of benzoic acid and either potassium hydroxide or potassium bicarbonate.

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SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED

DOCUMENT CONTROL DATA SHEET

REPORT NO.	AR NO.	REPORT SECURITY CLASSIFICATION
MRL-R-871	AR-003-060	UNCLASSIFIED

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REPORT DATE	TASK NO.	SPONSOR
February, 1983	ARM 80/220	Army

CLASSIFICATION/LIMITATION REVIEW DATE

CLASSIFICATION/RELEASE AUTHORITY
Superintendent, MRL Physical Chemistry Division

SECONDARY DISTRIBUTION

Approved for Public Release

ANNOUNCEMENT

Announcement of this report is unlimited

KEYWORDS

Pyrotechnics
Whistling compositions
Potassium benzoate
Differential scanning calorimetry
Thermal analysis
Thermochemistry

COSATI GROUPS 1901 0703

ABSTRACT

Potassium benzoate is one of the ingredients in the formulation SR 136 Whistling Composition. However, some ambiguity exists in the chemical literature as to its hydration state. In this investigation, it was established that potassium benzoate crystallizes from water as colourless plates containing no water of crystallization and it does not appear to take up water from its environment. Its DSC thermogram, over the temperature range 310 K - 750 K, consists of a single, sharp and symmetrical endotherm, occurring near 714 K and probably due to melting, the heat of this reaction being ca 213 J g^{-1} (50.9 cal g^{-1}). It can be prepared from stoichiometric amounts of benzoic acid and either potassium hydroxide or potassium bicarbonate.

POTASSIUM BENZOATE FOR PYROTECHNIC WHISTLING COMPOSITIONS : ITS SYNTHESIS AND CHARACTERIZATION AS AN ANHYDROUS SALT

1. INTRODUCTION

Certain pyrotechnic compositions, when compressed into a round tube and ignited, burn with a loud whistling noise (1-5) which results from rapid, periodic variations in very fast competing chemical reactions (1,3). One of the formulations chosen for study in these laboratories was that prepared according to British Ministry of Defence specifications (6) and called SR 136 Whistling Composition. It consists simply of a mixture of a vigorous oxidant, potassium perchlorate (ca. 70 per cent by weight), and a fuel, potassium benzoate (ca. 30 per cent by weight), and its properties have been described in some detail by Maxwell (1) and summarized by McLain in his recently published book (2).

Initial investigations were carried out on samples of SR 136 Whistle Composition and on samples of related compositions where the relative proportions of potassium perchlorate and potassium benzoate varied from those in SR 136. The results obtained confirmed that these preparations did indeed whistle, the acoustical output and the burning characteristics varying from composition to composition.

However, results from standard compositions prepared from different batches of materials were not always reproducible from batch to batch and some preparations were found to be prone to accidental or premature explosion (2,4,5,6). For these reasons, it was decided to look more closely at the properties of the components of these mixtures.

Potassium perchlorate is a well known ingredient in explosive formulations and the properties of the samples provided to us were very similar to those described in the literature (7) and found from authentic samples of potassium perchlorate (United States National Bureau of Standards

ICTA-DTA Standard Reference Material No. 758). The thermal data are presented in Table 1.

However, potassium benzoate is less well characterized. It is described in a U.K. Chemical Inspectorate Specification simply as "potassium benzoate, anhydrous" (8), an assignment confirmed by references to potassium benzoate found in Chemical Abstracts (9). On the other hand, it has also been referred to as a trihydrate (2,10) which loses its water of crystallization at 383 K (10).

It was to resolving this duality that the authors gave their attention and subsequently established that potassium benzoate crystallizes from water at 293 - 298 K (20-25°C) and also precipitates from aqueous alcohol as colourless plates, it does not contain water of crystallization and it melts near 715 K. It is suggested that the original description of potassium benzoate as a trihydrate (10) is wrong and that the sample, upon which this assignment was made, may have contained unreacted benzoic acid.

2. RESULTS

(a) General Investigation

Initially a sample of potassium benzoate was submitted to the authors to carry out routine measurements on the differential scanning calorimeter (DSC). At this stage, the authors believed that this sample was a trihydrate and the DSC trace subsequently obtained was consistent with this expectation. The trace showed two endotherms; one was asymmetric, commencing near 420 K with an extrapolated onset at 454 K and reaching a maximum energy uptake near 500 K; the other endotherm was sharp and symmetrical, reaching a maximum energy uptake near 714 K (Fig. 1).

The asymmetry of the low temperature endotherm was interesting, as it was different from any seen by the authors previously and corresponded very closely to that from a solid state decomposition reaction,

$$\text{Solid} \longrightarrow \text{solid} + \text{gas}$$

of reaction order $^1/_2$, the measured reaction order actually being 0.51_4 (11). Such a reaction order may be rationalised by assuming that the departing "gas" is escaping from a diminishing internal surface area (12).

From thermal gravimetric measurements carried out at 550 K, a weight loss of 15.1 ± 0.9% (average of six measurements) was observed. However, no further weight loss occurred below 750 K, the upper limit of our investigations. If potassium benzoate was originally present as a trihydrate (formula weight 214), a weight loss of 8.4% per molecule of water lost would have been predicted.

It was therefore decided to prepare and to authenticate a sample of potassium benzoate, to characterise some of its properties and to compare it to the original sample.

It was found that potassium benzoate prepared from stoichiometric amounts of either benzoic acid and potassium bicarbonate or benzoic acid and potassium hydroxide, recrystallizes from water and also precipitates from aqueous alcohol as colourless plates, it analyses as $C_6H_5CO_2^-K^+$, containing no water of crystallization and its DSC thermogram consists of a single, sharp symmetrical endotherm, melting near 715 K (Fig. 2). It is a stable compound and does not take up water when placed in a high humidity environment (Table 2). It is very soluble in cold water and the pH of an aqueous solution of potassium benzoate, 0.10 M was found to be 8.5_3, at 297 K, a value agreeing well with the calculated value, 8.60 at 298 K (13).

Subsequent inquiry revealed that the original sample had been prepared from weighed amounts of benzoic acid and potassium hydroxide, no allowance being made for the fact that potassium hydroxide was supplied in pellet form, assayed as "85% minimum content KOH".

Close inspection of the infrared absorption spectra (KBr discs) of authentic potassium benzoate and of the original sample of potassium benzoate indicated that there were real differences between the two samples and these could be attributed to the presence of benzoic acid in low concentration (Figs. 3-5). More complete analysis was carried out in the Organic Chemistry Division, MRL by Messrs. R.G. Davidson and G. Mathys on a Perkin Elmer 580B Infrared Spectrometer, using computer-assisted IR techniques. They reported:

1. both benzoic acid and potassium benzoate were soluble (to at least 0.5% w/v) in methanol,

2. the CO_2H carbonyl near 1700 cm^{-1} in benzoic acid and the asymmetric CO_2^- vibration near 1560 cm^{-1} in potassium benzoate were sufficiently well defined to allow analysis of mixtures of the two compounds using IR techniques (methanol as solvent, cell 0.05 mm path length, KRS-5 cell windows),

3. the original sample of potassium benzoate contained an estimated 12% (w/w) benzoic acid, and a synthetic mixture of benzoic acid and potassium benzoate (1:1 molar ratio), provided by Explosives Research Group, was analysed as containing 44% benzoic acid and 53% potassium benzoate (w/w) by this method, (theoretical 43% and 57%, respectively).

These results were confirmed by calorimetric studies.

Synthetic mixtures of benzoic acid and potassium benzoate were prepared and examined on the differential scanning calorimeter. The DSC traces in Figs. 6 and 7 confirmed that the low temperature endotherm in the original sample of potassium benzoate (Fig. 1) was due to the sublimation of benzoic acid from the crystal matrix and that the high temperature endotherm originated from potassium benzoate.

(b) Thermochemical Data

From differential scanning calorimetry, thermochemical data can be obtained to characterise the materials under investigation. The present study was no exception and in the Data Sheets 1-4 the thermochemical properties of potassium benzoate, benzoic acid and potassium benzoate - benzoic acid mixtures are summarized. These tables should be read in conjunction with the DSC traces presented in the various figures.

From these data, it is apparent that the original presence of benzoic acid in potassium benzoate (Data Sheet 1) does not alter the observed latent heat of melting of potassium benzoate around 714 K, 210 J g^{-1}; the authors assume that the low temperature endotherm observed in Figs. 1 and 7 is solely due to sublimation of benzoic acid from the crystal matrix and that, as a consequence, the crystal matrix of potassium benzoate is not altered by cocrystallized benzoic acid.

The temperature at which benzoic acid sublimes out of the crystal matrix, however, does appear to depend on its relative initial concentration. This will be the subject of a separate report.

3. CONCLUSIONS

The preparation of potassium benzoate is simple and straightforward. It can be prepared from benzoic acid and potassium bicarbonate or from benzoic acid and potassium hydroxide and crystallizes from water as colourless plates. Regular, small-particle-sized crystals of potassium benzoate can also be prepared directly by the controlled addition of potassium hydroxide in water to benzoic acid in methylated spirits.

In the differential scanning calorimeter, it undergoes a single endothermic reaction near 714 K when heated over the range 320 K - 750 K; the heat of the reaction for this endotherm is 213 ± 4 J g^{-1} (50.9 ± 1.1 cal g^{-1}). It exists as an anhydrous salt, $C_6H_5CO_2^-K^+$, and does not take up water when exposed to a high humidity environment at laboratory temperature and pressure.

Although it cocrystallizes with benzoic acid and forms a 1:1 mixture from water, there is no change in the latent heat of melting of potassium benzoate (per unit mass of potassium benzoate), within experimental uncertainty. This suggests that the mixture may not be a stoichiometric mixed salt with its own crystal identity but an "included salt", instead.

This could be established unequivocally by crystallographic studies.

4. EXPERIMENTAL

Materials

Benzoic acid was a BDH (A.R. grade) reagent, m.p. 393 - 395 K (120 - 123°C). It was used without further purification.

The original sample of potassium benzoate was a technical-grade reagent, prepared for use in the batch production of SR 136 Whistling Composition.

Synthesis

Potassium benzoate, (Method A). To a solution of benzoic acid (12.24 g, 0.10 mole) in ethanol (50 ml), potassium bicarbonate (10.0 g, 0.10 mole) in water (200 ml) was added with stirring, over a period of ten minutes. As expected, a brisk effervescence occurred (CO_2 liberation) and a copious white precipitate was formed. The mixture was taken to dryness under reduced pressure and water (100 ml) added to the mixture, which dissolved completely. The mixture was filtered and concentrated at ca. 60°C under reduced pressure (rotary evaporator) until the product started to precipitate out of solution. The mixture was then heated at ca. 80°C and allowed to cool. White crystalline platettes were obtained. The mother liquors were further concentrated to ca. 15 ml and yielded further material, identical with the first batch, except that it was amorphous. Analysis (AMDEL, Australian Microanalytical Laboratories, Ref. 8858, Feb. 1982) C 52.43%, H 3.13%, O 20.3%; calc. for potassium benzoate $C_7H_5O_2K$, C 52.47%, H 3.14%, O 19.97%.

Potassium benzoate was characterized as described in this report.

Identical material was prepared using stoichiometric amounts of potassium hydroxide and benzoic acid.

Potassium benzoate, (Method B). The following method was used to prepare small particle sized potassium benzoate, conforming to specifications defined for the preparation of SR 136 Whistling Composition (1,6), directly and without requiring mechanical grinding of the product. Such specifications require potassium benzoate to be able to pass through British Standard Sieves 170 (90 micron) or 120 (125 micron).

Benzoic acid (600 g, 4.918 mole) was added to methylated spirits (2 l) in a 10 litre stainless steel pot. The solution was stirred at 25-30 rpm until all the benzoic acid had dissolved. A solution containing a stoichiometric amount of potassium hydroxide in 200 ml water was added through a separating funnel over a period of two minutes - the addition time being critical in obtaining a product of the correct particle size. Potassium benzoate precipitated out during this addition process but the stirring was continued for a further ten minutes.

The product was filtered off under vacuum (Buchner funnel) and thoroughly dried at the pump. This mass was broken up, spread on a tray and further dried in an oven at 65°C. Yield approx. 550 g (70%). This material analysed satisfactorily for potassium benzoate, anhydrous and was identical (IR and DSC measurements) with that obtained by Method A.

Comparative particle-size analyses were carried out using scanning electron microscopy (Mrs V. Silva, Physics Division, Materials Research Laboratories). These indicated that this method consistently gave material of an acceptable size, (Fig. 8).

Potassium benzoate : benzoic acid (1:1 molar ratio). To a solution of benzoic acid (12.20 g, 0.10 mole) in ethanol (100 ml), potassium benzoate (16.00 g, 0.10 mole) in water (500 ml) was added and the mixture heated on a steam bath to dissolve up the precipitate formed. The mixture was concentrated to ca. 50 ml (rotary evaporator) and cooled. A fluffy white precipitate (ca. 4 g) which formed was filtered off and dried at the pump. Infra-red analysis indicated that it consisted of a mixture of benzoic acid and potassium benzoate in equimolar proportions. Thermal gravimetry (at 550 K) indicated that the mixture consisted of potassium benzoate : benzoic acid (0.55_7 : 0.44_3 w/w or 1:1.02 molar ratio), a result confirmed by differential scanning calorimetry. The DSC thermogram for this mixture showed a very small endotherm near 393 K (120°C), attributed to the excess benzoic acid (2%) and two endotherms at 513 K (240°C) and 716 K (443°C) attributed to benzoic acid and potassium benzoate respectively, coprecipitated in equimolar proportions. Its IR spectrum is presented in Figure 9.

Determination of the Hydration State of Potassium Benzoate

The following method was used originally to establish the formation of a stable hydration state for sodium 2-nitrotetrazole, namely the dihydrate, from the anhydrous salt, under normal laboratory conditions (14). Here, the same technique was applied to potassium benzoate to ascertain if it also took up water in a similar manner; it did not.

Potassium benzoate was broken up and dried to a constant weight in an air-oven at 140°C (413 K) and six samples, each of ca. 0.1 g, weighed into six tared weighing bottles. Three of these were set aside for reference. To the remaining bottles, water (ca. 0.1 g) was added directly onto the samples, sufficient to enable a trihydrate to form, if indeed it could form under these conditions.

One of these latter samples and one of the reference samples were placed in each of the three "constant humidity" desiccators prepared for this test:-

Desiccator	Medium	Humidity Range (%)	Temp. Range (°C)
A	satd. $CaCl_2.6H_2O$	31 - 35	18.5 - 24.5
B	satd. $Mg(NO_3)_2.6H_2O$	52 - 56	18.5 - 24.5
C	satd. NH_4Cl	78 - 80	20 - 30

and changes in weight monitored at regular intervals. The tests were deemed completed when there was no further change in weight observed in each of the test and reference samples.

These results are summarized in Table 2 and were consistent with the conclusion that potassium benzoate does not form a hydrate under these conditions.

Thermal Analysis

Thermograms were measured on a Perkin Elmer Differential Scanning Calorimetry Apparatus, Model DSC-2, equipped with a Scanning Auto Zero Accessory. The output of the DSC-2 was calibrated using samples of indium (15,16). Indium has a very sharp melting point (429.7 K, 156.6°C) and a latent heating of melting of 28.46 J g^{-1} (6.80 cal g^{-1}).

Samples (usually ca. 1 mg) were weighed into aluminium sample pans, capped and placed in the DSC apparatus. Nitrogen gas continuously purged the sample and reference compartments throughout the runs which were typically carried out at a heating rate of 40 K min^{-1} over the temperature range 310 K - 750 K.

Samples were weighed on a tared Mettler ME30 Microbalance, before and after each run, when weight-loss experiments were being carried out. These results were supplemented by thermal gravimetric analysis carried out on either a Dupont 1090 TGA apparatus (Dr. B. Ennis, Organic Chemistry Division) or a Perkin Elmer TGS-1 Thermobalance (Mr. M. Parry, Physical Chemistry Division).

All results quoted are the average of at least five experiments.

Infrared Spectra

Routine infrared spectra were measured on either a Pye-Unicam SP 1000 Infrared Spectrophotometer or a Perkin Elmer IR 683 Infrared Spectrometer.

More complete analyses were carried out by Messrs. R.G. Davidson and G. Mathys (Organic Chemistry Division) on a Perkin Elmer 580B Infrared Spectrometer.

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TABLE 1

DSC CHARACTERISTICS OF POTASSIUM PERCHLORATE

(EX MRL) OVER THE TEMPERATURE RANGE 310 K - 750 K

Heating Rate	:	40 K min^{-1}
Thermogram	:	Single endotherm; no exothermic reaction observed over temp. range
Characteristics of Endotherm :		
Phase transition onset (rhombic/cubic)		572 K (299°C)
Temperature of maximum energy uptake		576 K (303°C)
Heat of Transition		97.3 ± 1.7 J g^{-1} (23.30 ± 0.4 cal. g^{-1})

T A B L E 2

THE HYDRATION STATE OF POTASSIUM BENZOATE UNDER NORMAL LABORATORY CONDITIONS

Relative Humidity	32%		52%		79%	
Sample	L	X	M	Y	N	Z
Mass benzoate dry	0.0984	0.0971	0.0978	0.1028	0.1009	0.0961
Mass added water	0.0853	-	0.1002	-	0.1103	-
Total mass	0.1837	0.0971	0.1980	0.1028	0.2112	0.0961
Variation in Mass						
38 days	-0.0837	+0.0016	-0.0990	+0.0001	-0.1087	+0.0014
51 days	-0.0841	+0.0007	-0.0998	0.0000	-0.1094	+0.0005
65 days	-0.0840	+0.0009	-0.0995	-0.0003	-0.1092	+0.0007
Uptake	+0.0014	+0.0009	+0.0008	-0.0003	+0.0011	+0.0007
% (w.r.t. benzoate)	1.4	0.9	0.8	-0.3	1.1	0.7

1. All masses in g.

2. Over a period of 65 days, the samples L, M, N lost all but an insignificant amount of added water to the surroundings. At the same time, the reference sample X, Y, Z did not gain any weight. Hence, under these conditions, potassium benzoate appears stable in the unhydrated form.

DATA SHEET 1

DSC CHARACTERISTICS OF ORIGINALLY-SUBMITTED

SAMPLE OF POTASSIUM BENZOATE, (FIGURE 1)

1. Thermal gravimetry established that this sample contained 15.1 ± 0.9% (by weight) unreacted benzoic acid.

2. There were two endotherms observed in the temperature range 320 K - 750 K.

3. The first endotherm was unsymmetrical, the onset temperature occurring at 454 K (181°C) with a temperature of maximum energy uptake at 504 K (231°C). This was attributed to sublimation of benzoic acid from the mixture and the heat of transition calculated per gram of benzoic acid was 803 ± 13 J (192 ± 3 cal).

4. The second endotherm was symmetrical. The onset temperature occurred at 711 K (438°C) and the temperature of maximum energy uptake at 716 K (443°C). This was attributed to melting of potassium benzoate and the heat of transition calculated per gram of benzoate was 213 ± 4 J (50.9 ± 1.0 cal).

DATA SHEET 2

DSC CHARACTERISTICS OF POTASSIUM BENZOATE OVER THE TEMPERATURE RANGE 320 K - 750 K (FIGURE 2)

1. Single endotherm.

2. At a heating rate of 40 K min^{-1}, the onset temperature (melting point) occurred at 710 ± 1 K (437°C) and the temperature of maximum energy uptake occurred at 714 ± 1 K.

3. The heat of transition, determined by integration of the area under the DSC thermogram, was 213 ± 5 J g^{-1} (50.9 ± 1.4 cal. g^{-1}).

DATA SHEET 3

DSC CHARACTERISTICS OF BENZOIC ACID OVER THE

TEMPERATURE RANGE 320 K - 550 K (FIGURE 6)

1. At a heating rate of 40 K min^{-1}, two endotherms were observed.

2. The properties of the first endotherm were as follows:

   (a) symmetrical energy uptake

   (b) Onset temperature (melting), 393 K (120°C)

   (c) Temperature of maximum energy uptake occurred at 397 K (123°C)

   (d) The heat of transition was ca. 146 ± 21 J g^{-1} (35 ± 4.5 cal g^{-1}, lit. 34 cal g^{-1}, Ref. 16).

3. The second endotherm superimposed the first. It had an unsymmetrical temperature uptake.

The extrapolated onset temperature was ca. 435 K (162°C) and the temperature of maximum energy uptake occurs near 480 K (207°C). The heat of transition is ca. 585 ± 42 J g^{-1} (140 ± 10 cal g^{-1}, lit. 139 ± 6 cal g^{-1}, Ref. 17).

These results were the least reproducible of all those carried out; benzoic acid sublimes somewhat, even below its melting point, and, under the conditions described here, a drift-free base-line is difficult to obtain.

DATA SHEET 4

DSC CHARACTERISTICS OF POTASSIUM BENZOATE : BENZOIC ACID (1:1.02 MOLAR RATIO) OVER THE TEMPERATURE RANGE 320 K - 750 K (FIGURE 7)

1. Three endotherms observed, at a heating rate of 40 K min^{-1}.

2. First endotherm corresponded to *ca.* 2% free benzoic acid in the mixture and occurred near 393 K (120°C).

3. The second endotherm, corresponding to the sublimation of coprecipitated benzoic acid from the mixture, was unsymmetrical. The onset temperature occurred at 477 K (404°C) and temperature of maximum energy uptake occurred at 513 K (240°C). The heat of transition per gram of benzoic acid was 819 ± 15 J (195.7 ± 3.5 cal).

4. The third endotherm, corresponding to the sublimation of coprecipitated potassium benzoate, was symmetrical. The onset temperature occurred at 712 K (439°C) and the temperature of maximum energy uptake occurred at 716 K (443°C). The heat of transition per gram of potassium benzoate was 210 J (50.5 cal).

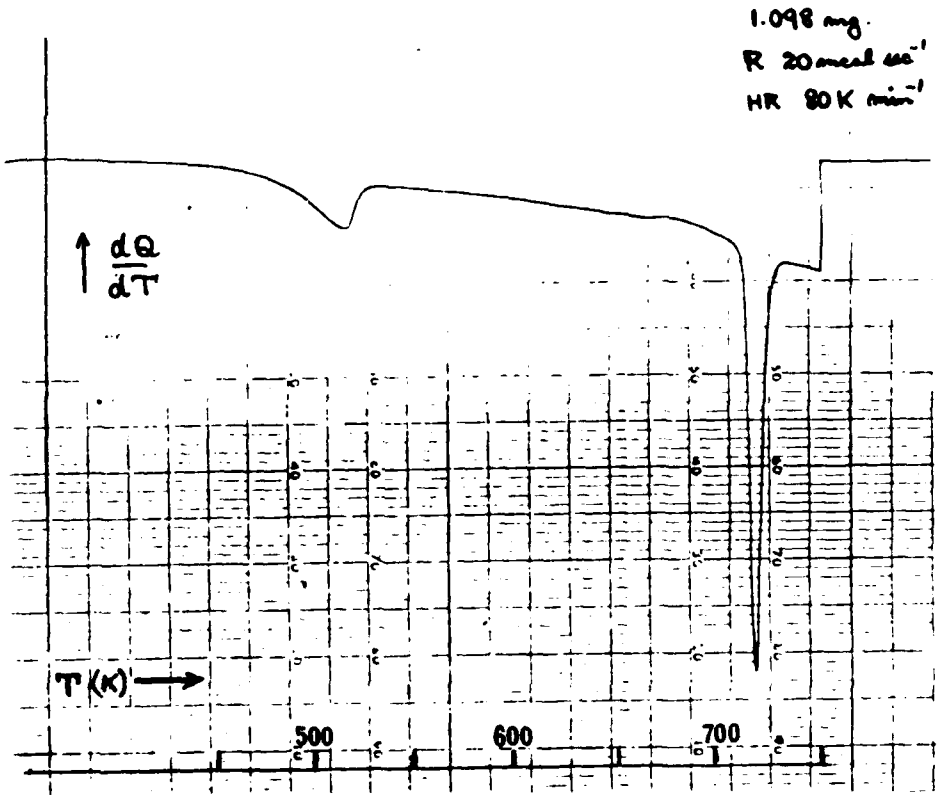

FIG. 1. DSC trace of the originally-supplied sample of potassium benzoate, submitted for routine analysis. The low temperature endotherm is due to benzoic acid (15.1%, w/w) impurity. Refer *Data Sheet 1*.

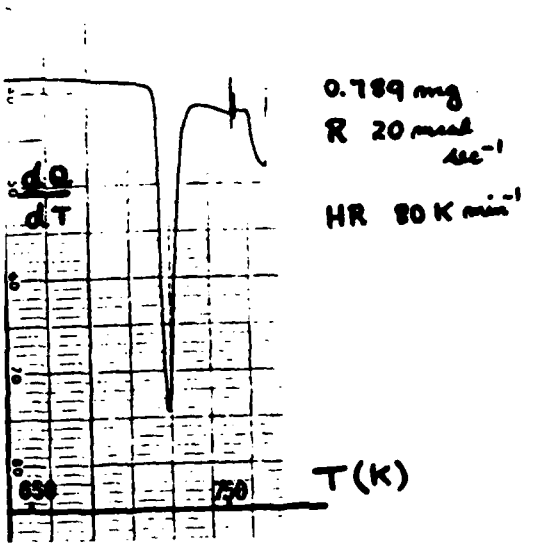

FIG. 2. DSC trace of analytically-pure potassium benzoate, prepared by the authors. Refer Data Sheet 2.

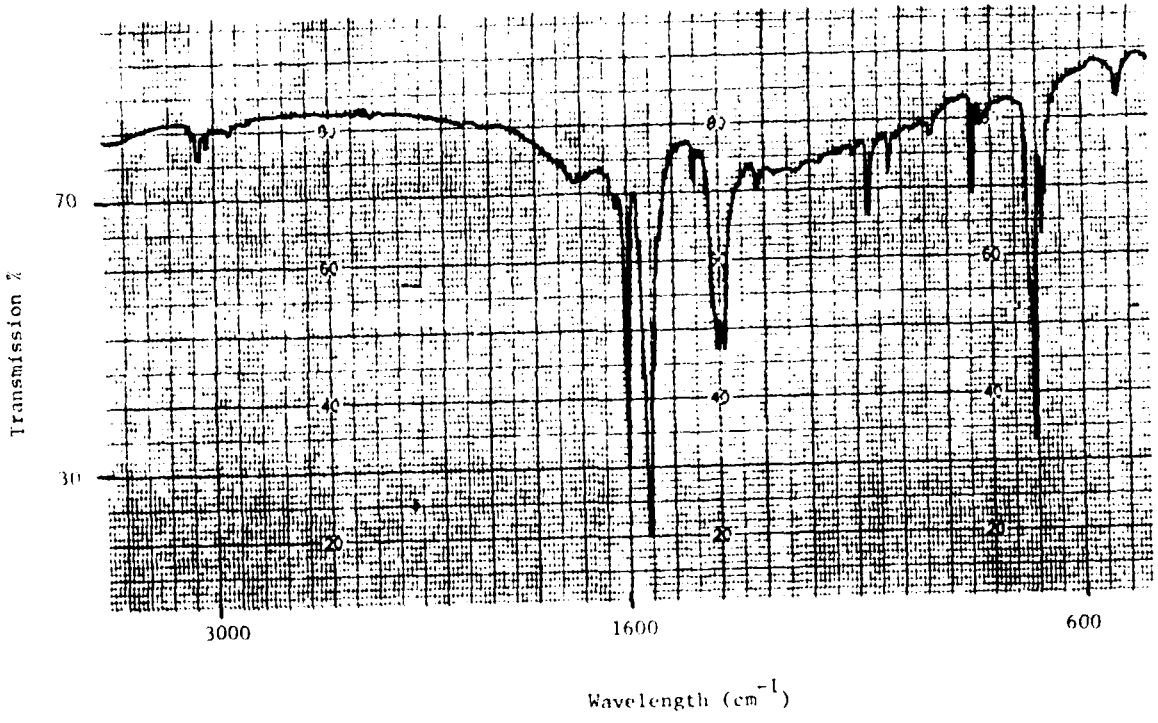

FIG. 3. IR spectrum (KBr disc) of the originally-supplied sample of potassium benzoate, containing 15.1% (w/w) benzoic acid.

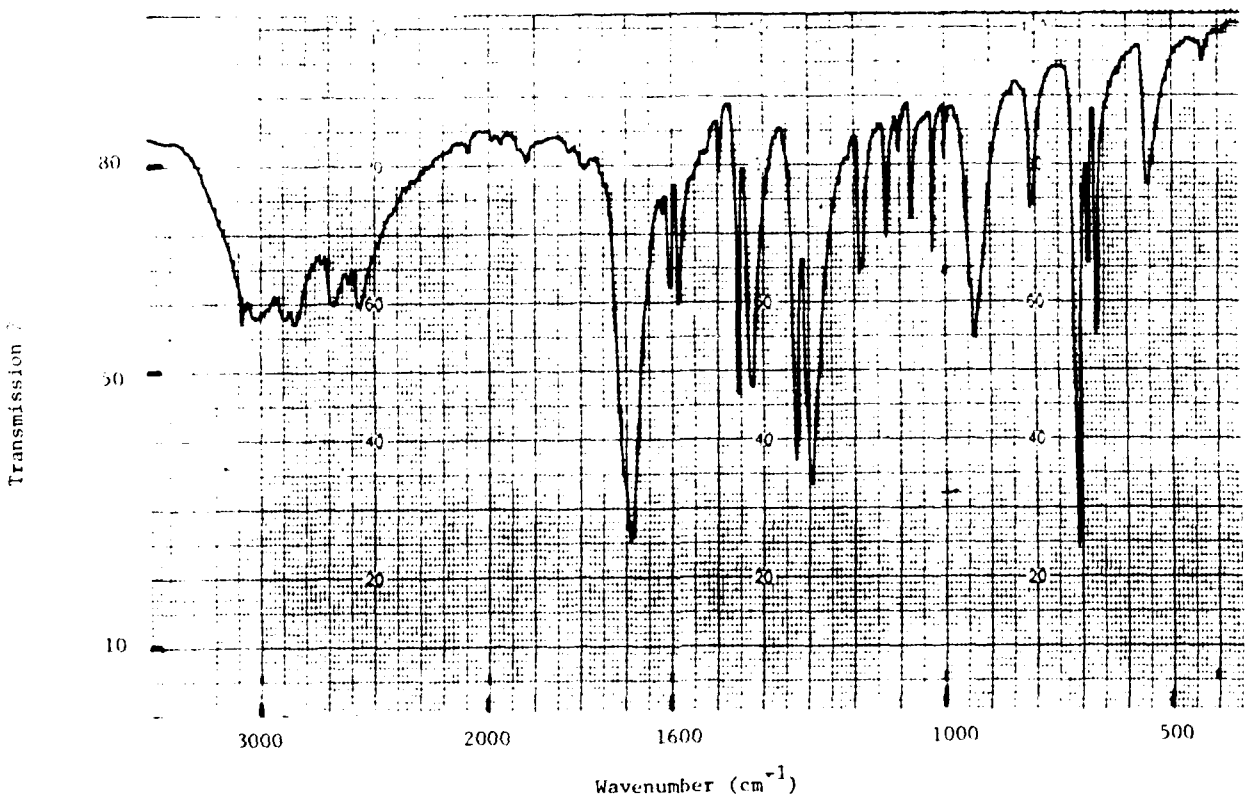

FIG. 4. IR spectrum (KBr disc) of benzoic acid.

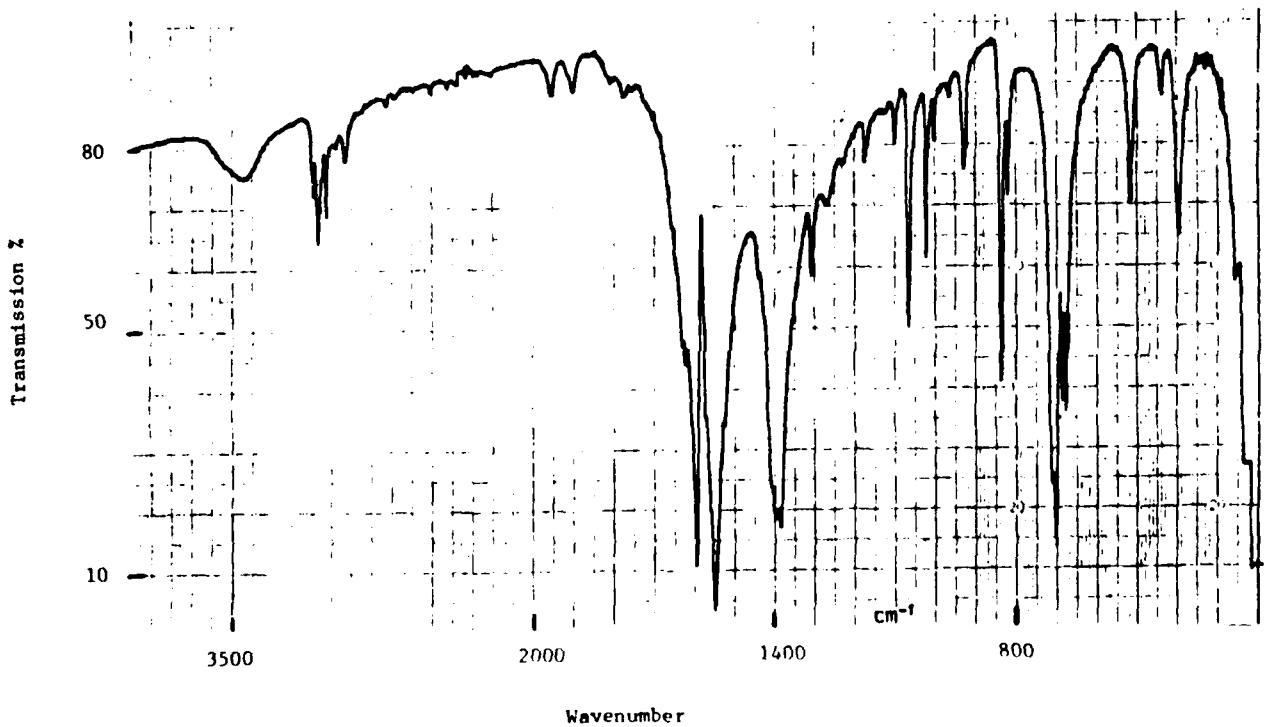

FIG. 5 IR spectrum (KBr disc) of potassium benzoate.

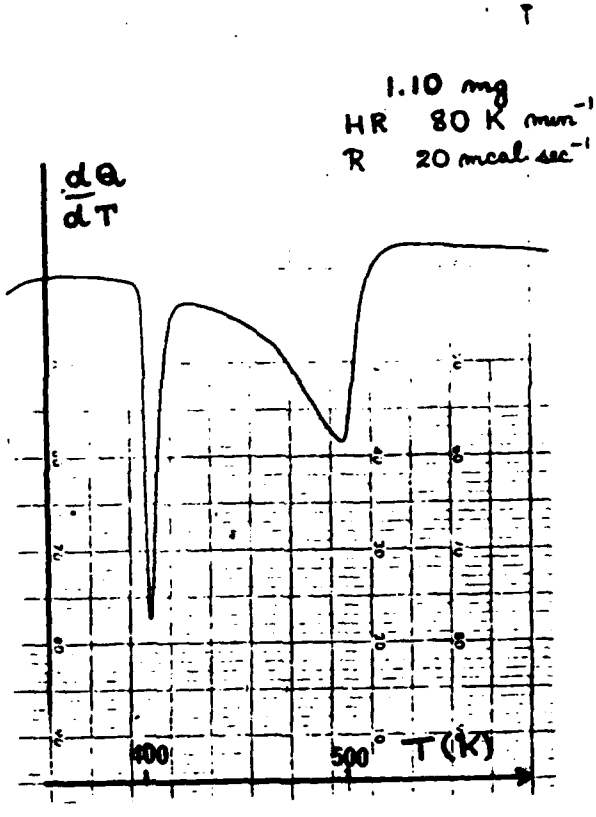

FIG. 6. DSC trace of benzoic acid, Refer Data Sheet 3.

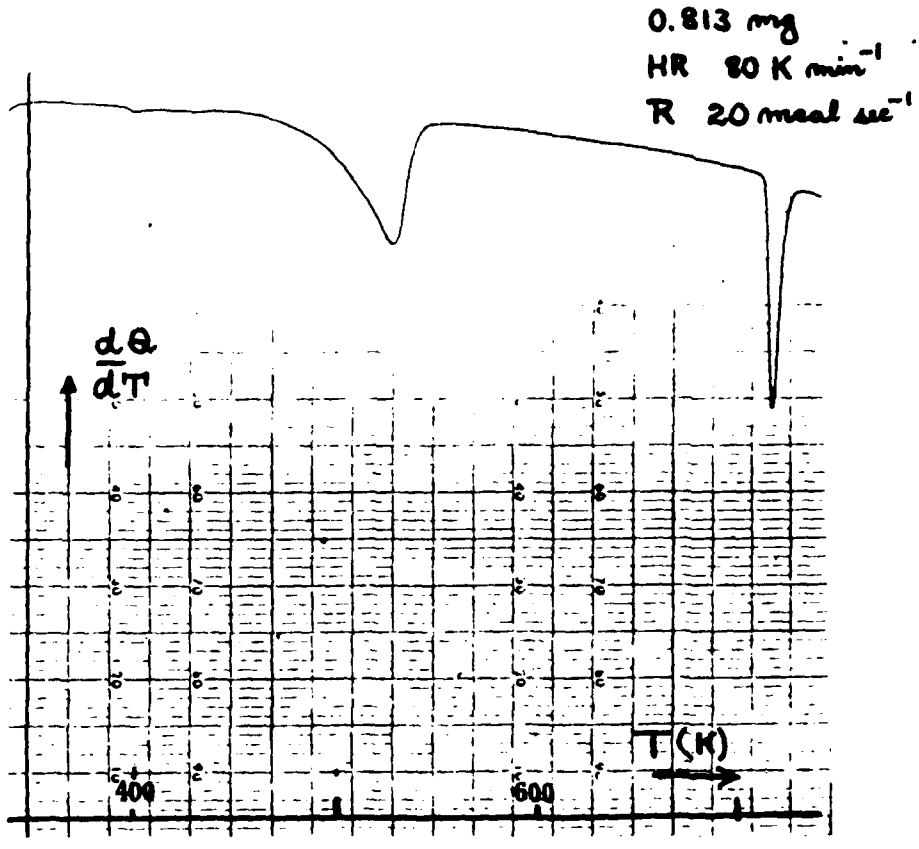

FIG. 7. DSC trace of benzoic acid - potassium benzoate (1.02: 1 molar ratio). Refer Data Sheet 4.

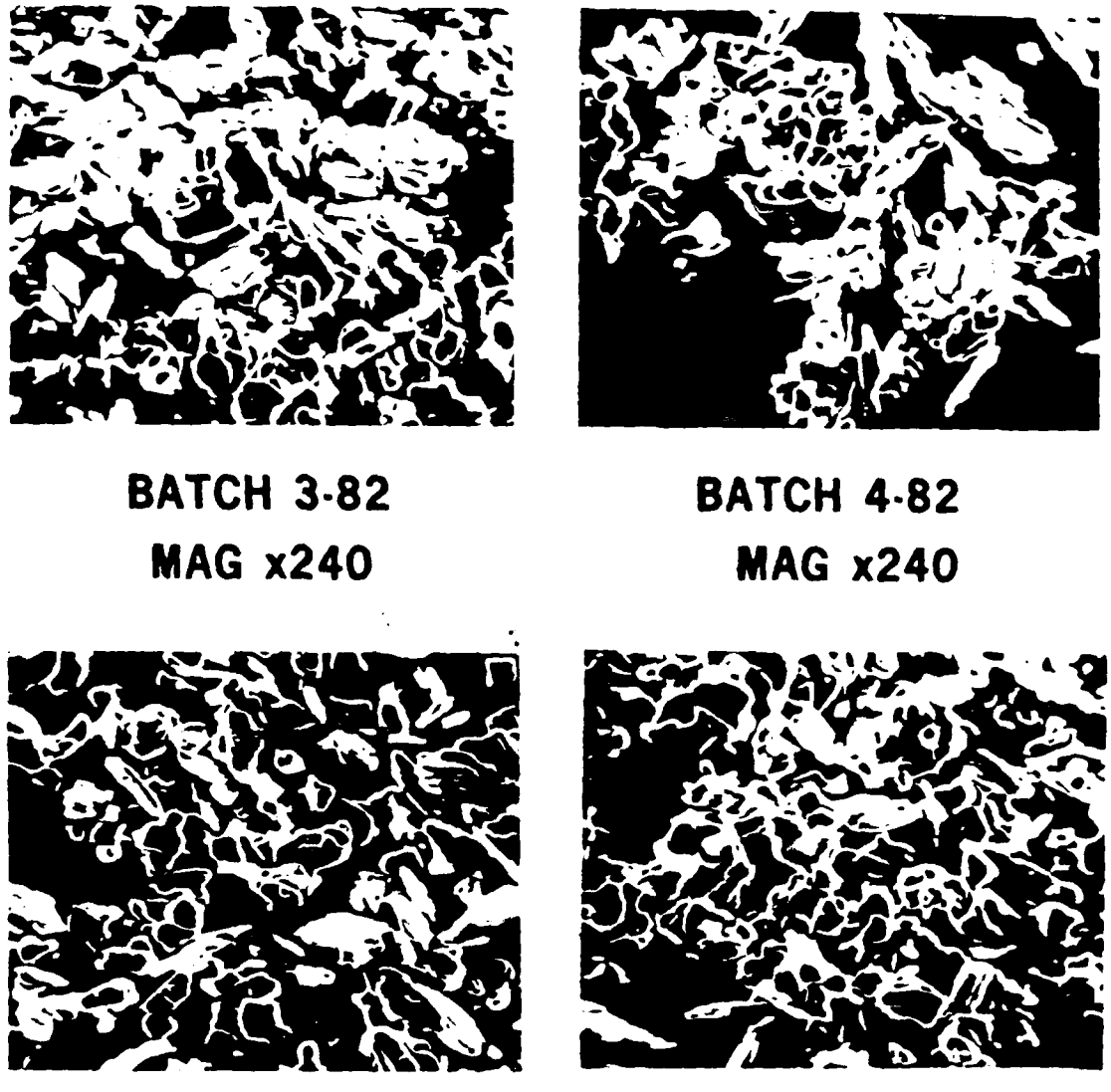

FIG. 8. Comparative particle-size analysis of potassium benzoate from scanning electron microscopy.

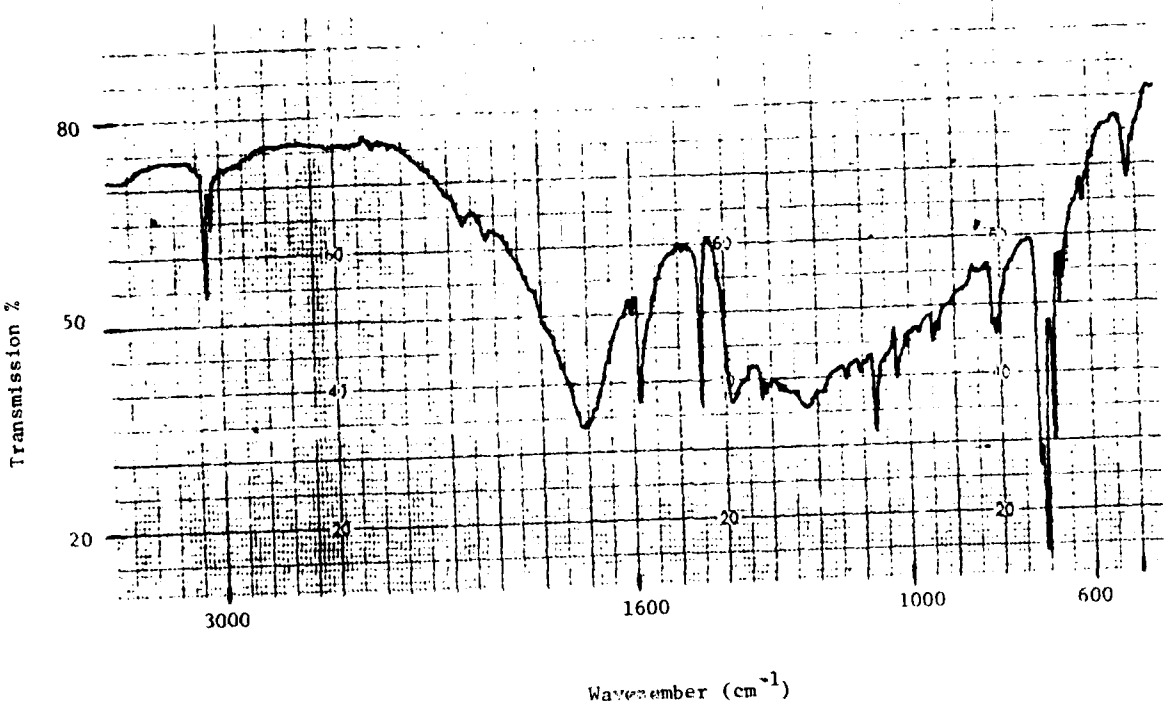

FIG. 9. IR spectrum (KBr disc) of benzoic acid - potassium benzoate (1.02 : 1 molar ratio).

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